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13. ABSTRACT (Maximum 200 words)
Our Phase I work demonstrated the feasibility of a mobile LIBS system for the detection of biological agents. This is a very demanding application, in part because of the need to detect threat particles in the presence of a much larger number of benign particles. We believe that the best solution to this problem lies in particle beam focusing technology developed at Aerodyne Research for use in other aerosol analysis devices, most notably a commercially successful aerosol mass spectrometer. Using this aerodynamic lens technology, a large fraction of the total particles sampled can be brought to the focal point of a LIBS excitation laser. Therefore, our goal in Phase I was to demonstrate the feasibility of an aerosol particle sampling/microchip laser LIBS system for biological agent detection. The microchip laser is currently the only LIBS-capable laser that can operate at the kHz repetition rates needed for detection of trace fractions of particles in a reasonable amount of time. Other advantages of microchip lasers include small size, rugged construction, low power consumption and, most importantly, the ability to be triggered. Key issues addressed in Phase I work were the choice of spectral detection regions, an assessment of the microchip laser power requirements, and a demonstration of the use of aerodynamic focusing and laser triggering to enhance sensitivity.

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1. Introduction

Our Phase I work demonstrated the feasibility of a mobile LIBS system for the detection of biological agents. Biological agent detection is a very demanding application, in part because of the need to detect threat particles in the presence of a much larger number of benign particles.[1] If a detection method is used that generates signals from all particles, both target and background, as is the case with LIBS, there are two possible strategies to deal with this problem. One is to collect a large number of particles, obtain high quality spectra, and use sophisticated analysis techniques to extract the contributions of a few target particles from those of a much larger number of background particles. The second strategy, which we are pursuing, is to interrogate individual particles. We believe the particle beam focusing technology developed at Aerodyne Research for use in other aerosol analysis devices, most notably a commercially successful aerosol mass spectrometer, is the best way to bring a large fraction of the total particles sampled to the focal point of a LIBS excitation laser. Furthermore, the microchip laser is currently the only LIBS-capable laser that can operate at the kHz repetition rates needed for detection of trace fractions of particles in a reasonable amount of time. Other advantages of microchip lasers include small size, rugged construction, low power consumption and, most importantly, the ability to be triggered. This last attribute allows the use of light scattering signals from upstream laser diodes to fire the microchip LIBS excitation laser to substantially increase the odds of hitting a particle to near unity.

Therefore, our goal in Phase I was to demonstrate the feasibility of an aerosol particle sampling/microchip laser LIBS system for biological agent detection. Two key innovations in the proposed system intended to maximize detection sensitivity and discrimination were studied. The first was the use of the aforementioned microchip laser excitation source. The second innovation concerned the use of an aerodynamic lens collimator for aerosol sampling, a component which effectively increases the concentration of particles within the LIBS apparatus. Key issues addressed in Phase I work were the choice of spectral detection regions, an assessment of the microchip laser power requirements, and a demonstration of the use of aerodynamic focusing and laser triggering to enhance sensitivity. This work was done in collaboration with research groups at the University of Florida headed by Profs. Winefordner and Hahn.

2. Background and Motivation for Phase I Technical Approach

The key background areas for this program are biological agent detection, the LIBS technique, and two important enabling technologies, the microchip laser, and the aerosol inlet and focusing lens. We will discuss each in turn.

Biological Agent Detection

We cannot state any more clearly the basic issues involved in the detection of biological agents than does the following excerpt from a recent article in the Lincoln Laboratory Journal:[1] "By far the most effective method for a biological attack is to dispense the bioagent as aerosol particles in the air. The bioagent particles then float in the air until they are inhaled. Aerosol attacks have two major advantages: (1) the bioagent particles are naturally dispersed in the atmosphere and, driven by the wind, can drift over large areas, and

(2) many diseases are more virulent when spread by the aerosol route. For maximum effect it is generally agreed that the bioagent particles should be in the size range of 1 to 10 μm. Larger particles will precipitate out of the air in too short a time; smaller particles will tend to be expelled from the lungs."

With this in mind, our program focused on detection of biological agent aerosol particles in a sampled airstream. This approach differs from other possible approaches, such as collection on filters followed by LIBS analysis, in being truly real-time and involving the least interference with the sample. While filter collection has the potential advantage of integrating the signal from target particles, it may in fact exchange the airborne sampling scenario, of a LIBS signal from either one target or one background particle, for a less appealing one. Signal from any target particles could always be accompanied by signal from several more background particles. Then, interrogating a filter surface using LIBS could result in such strong signals from background particles that it is never possible to isolate weaker signals from a few biological particles.

A focus on detection of particles suspended in an airstream does not, however, mean that the device we propose will be only useful as a warning device. The application of monitoring surfaces for contamination may also be best accomplished not by direct LIBS on the surfaces, but rather by vacuuming the surfaces and examining whatever particles can be removed from the surface. This is because the small areas sampled by LIBS using even the highest power lasers mean that a significant surface concentration of small particles could be missed in a finite sampling time. If entrainment in an airflow brings almost all particles into the laser interaction region, as we propose, it will be possible to have greater confidence that this surface-screening application can be performed efficiently.

Laser-Induced Breakdown Spectroscopy

Although LIBS has been studied for almost three decades, the major breakthroughs, both in science and technology, have come only in the last few years, as evidenced by the explosive growth of the literature.[2-4] The LIBS technique is similar to a number of other analytical techniques involving plasma excitation of atomic emission lines, with the difference that it requires little or no sample preparation. An excitation laser is focused on the sample to be analyzed, a small volume of material is ablated, and the vaporized atoms are excited in a small region of plasma created by the laser excitation. This emission from neutral atoms and ions, which provides the composition analysis information, is initially masked by continuum plasma emission, but has a longer lifetime, so that either time gating or time integration can be used to extract the desired signals. The emitted light is spectrally resolved, and ratios of emission line intensities can be used to determine elemental composition. Occasionally, molecular emission bands are observed, although these may be from molecules formed as the plasma recombines or reacts with the ambient atmosphere.

Among the advantages of LIBS are its ability to deal with unprepared samples, its essentially nondestructive nature due to the small volume of material sampled, and its speed and simplicity, allowing real-time analysis. Among the drawbacks experienced in past applications have been: the need for a powerful excitation laser, poor precision due to

sensitivity to surface properties and their variations, difficulties in quantification, and inadequate detection limits. One major innovation of this proposal, the use of a microchip laser, addresses the first issue. The last three are less critical here, as biological agent detection may rely less on absolute quantification and more on a qualitative comparison to a known, finite set of spectral "fingerprints".

Microchip Lasers

The diode-pumped, passively Q-switched microchip laser was invented by John J. Zayhowski of the MIT Lincoln Laboratory.[5,6] The laser consists of an approximately 1-mm^3 Nd:YAG laser chip and a Cr:YAG Q-switching chip. The laser cavity mirrors are vapor deposited directly on opposing sides of the crystals. The laser is pumped through an optical fiber by a conventional 808-nm diode laser. Further chips of nonlinear optical materials can be added to give microchip lasers emitting at various harmonics, but our focus here will be on the simplest and most powerful lasers operating at the fundamental wavelength of 1064 nm. Standard microchip lasers following the Lincoln Laboratory design, produced under license and sold in the United States by JDS Uniphase, produce pulse energies of more than 6 μJ, at repetition rates of 2-5 kHz. The University of Florida used a JDS Uniphase laser in its Phase I work. Microchip lasers produced by Litton Poly-Scientific have a different design, with the pump laser and microchips contained inside a TO-3 package of the sort used for power transistors. The Litton Poly-Scientific laser we used in Phase I delivered 11 μJ per pulse at 8 kHz. Much higher pulse energies are possible. The JDS Uniphase PowerChip laser, pumped by a diode laser array, produces pulses with energies of up to 50 μJ, and Litton Poly-Scientific has tested a prototype up to 220 μJ with the expectation of higher powers as development continues.

Microchip laser pulses are near-diffraction limited and of sub-nanosecond duration. An important feature of these passively Q-switched lasers is that their pulse energy is independent of fluctuations in the pump laser power. In principle, such fluctuations would affect the repetition rate of the laser instead, but in practice the pump laser can be switched on and off at a fixed frequency, so that the pulses are very stable both in intensity and repetition rate. This will be a key issue in the current application, as will be discussed below.

Microchip lasers have a number of advantages for LIBS applications. The short (typically around 500-psec width) pulses have proved to be significant in producing plasma emission with a superior line-to-background-continuum ratio.[7] The laser system is very compact and lightweight, with current commercial versions weighing under 2.5 kg. Power requirements are also moderate. The laser has no moving parts or adjustments and is quite rugged, making it ideal for portable field instruments.

Focused Aerosol Particle Beams

A key component of Aerodyne's aerosol mass spectrometers is a unique aerodynamic particle lens developed at the University of Minnesota.[8,9] This device continuously samples ambient aerosol at a flow rate of about 100 sccm and focuses particles into vacuum in a beam about 0.1 mm in diameter. For particles in the 0.05 to ~2 • m diameter size range this lens

operates with nearly 100% transmission efficiency, verified in our current work through fluid dynamics modeling and experimental observations.[10-12] Recently, we have begun experimental and calculational work to improve the transmission of particles in the 1 to 10 • m size range, which has already resulted in improvements in the inlet to the lens, and is expected to result in adequate transmission throughout the size range of interest to us here. An important property of aerodynamic focusing is that fact that the final particle velocities are dependent on the size, with lighter particles being faster. This means that a laser light scattering beam that times particles to provide a trigger for the LIBS excitation laser can also provide particle size information. We have been implementing such a scheme as a retrofit to our aerosol mass spectrometers, using a testbed apparatus described below.

3. Phase I Work Statement

The goal of Phase I work is to demonstrate the feasibility of a biological agent aerosol detector using microchip laser excitation and aerodynamic focusing of a particle beam. To that end, Aerodyne Research will perform the following tasks:

Task 1. Assemble a laboratory demonstration laser-induced breakdown spectroscopy (LIBS) apparatus, including a microchip laser, spectrometers, optical and mechanical components, and a data acquisition system. This task will be shared between Aerodyne Research and the University of Florida.

Task 2. Utilize the LIBS apparatus to obtain spectra for a variety of samples and apparatus parameters, and analyze the spectra to determine feasibility of biological agent detection using LIBS. This task will be carried out primarily at the University of Florida.

Task 3. Assemble a second apparatus consisting of a microchip laser, a particle inlet and aerodynamic lens, triggering lasers, photodiode detectors, and associated electronics and data acquisition systems, for the purpose of characterizing the interaction of a microchip laser excitation source with an aerosol particle beam. This task will be carried out at Aerodyne Research.

Task 4. Utilize the microchip laser/aerosol sampling apparatus to investigate the overlap between excitation laser beam and aerosol particle beam, and the resulting laser power requirement for sensitive detection. In addition, characterize the triggering uncertainty inherent in the microchip lasers available during Phase I. This task will be carried out at Aerodyne Research.

Task 5. Analyze the results of all laboratory experiments to determine a conceptual design of a portable, microchip-laser-based LIBS instrument capable of detecting biological agent aerosols. The design will include a set of specifications for all hardware components of the instrument, and a discussion of automated data analysis algorithms to process LIBS spectra and other measurements to identify target particles and discriminate against background signals.

4. Phase I Results

Task 1. Assemble a laboratory demonstration LIBS apparatus

We did in fact operate complete LIBS apparatuses at both Aerodyne Research and the University of Florida. Both setups used Ocean Optics miniature spectrometers, and differed in the microchip laser used, with Aerodyne using one from Litton Poly-Scientific, and the University of Florida using one from JDS Uniphase. The Aerodyne apparatus was used only to check that the optics and substrates we planned to use in the particle beam experiments would give good LIBS signals. The University of Florida apparatus was used to carry out the main work of Task 2, an extensive series of experiments to characterize the time and spatial characteristics of microchip laser LIBS.

Task 2. Obtain LIBS spectra to determine feasibility of biological agent detection

As we began Phase I we determined that there was existing and ongoing work[13-16] using conventional LIBS to show the ability to discriminate between bioagent and background spectra. We realized that the most important thing we could do would be to establish that microchip LIBS was capable of delivering spectra of similar quality, in terms of signal-to-noise, bulk sampling, reproducibility. Therefore, the microchip laser characterization work at the University of Florida used a wide variety of substrates whose behavior in conventional LIBS was well known, and took data on the spatial, spectral and temporal aspects of microchip laser LIBS. Figure 1 shows some of the apparatus used in this work.

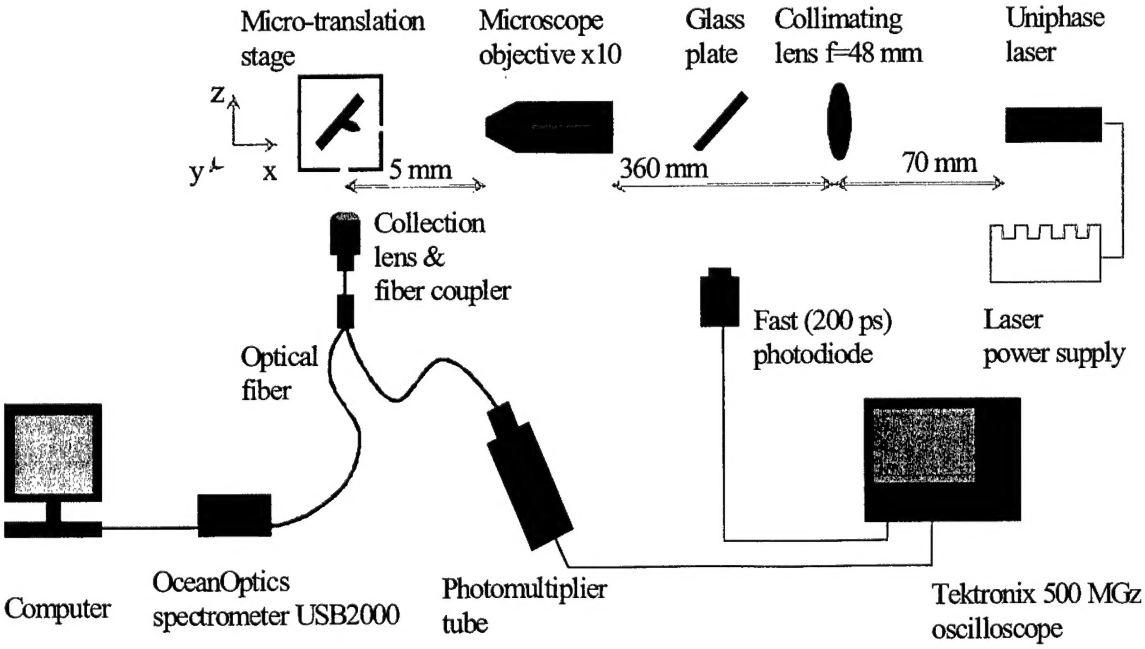

Figure 1. Apparatus used in microchip laser characterization work at the University of Florida.

One result which highlights a significant difference between conventional LIBS and LIBS with microchip lasers is the duration of the plasma emission. University of Florida's measurements show that the optical emission of the plasma is not much greater than the duration of the laser pulse. Their measurements suggest that a 500 ps laser pulse produces a plasma which emits for about 1 ns (the JDS Uniphase nominal specification for laser pulse width is 700 ps). Figure 2 shows the laser pulse width. They are considering ways to further improve the time resolution of these measurements, but the important qualitative differences with conventional LIBS are already clear. The plasma emission pulse obtained with this 10 • J pulse energy microchip laser is enormously shorter than the ca. 10-50 • s plasma emission which one obtains with 50 mJ pulse energy, 5 ns pulse width lasers. Put another way, although microchip lasers are up to 4 orders of magnitude lower in pulse energy or 3 orders of magnitude lower in peak power, the plasma duration is up to 5 orders of magnitude shorter. It is interesting to note that the power density for the microchip laser (10 uJ, 500 ps, 10 um focus diameter), 25 GW/cm^2 is only about 20X smaller than what is normally used for conventional LIBS (50 mJ, 5 ns, 100 um focus diameter), 130 GW/cm^2.

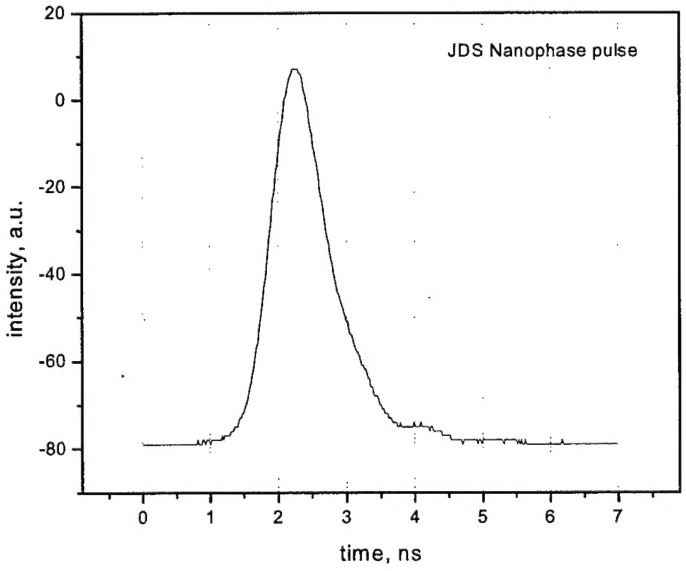

Figure 2. Photodiode measurement of microchip laser pulse. Even this instrumentation broadens the pulse, so this measurement is consistent a pulse width of 500 ps. Measurements to date are consistent with a LIBS plasma duration of no longer than 1 ns.

Another key area of investigation by the University of Florida group has been the volume of material removed from the substrate by microchip laser LIBS. They have made many micrographs of trenches formed on slowly moving substrates and of single-pulse craters made on faster moving surfaces. An example is shown in Figure 3. These show

crater dimensions and morphology varying with the material, with larger, rougher craters formed in low melting point materials and smaller, smoother craters in refractory materials. Example crater diameters vary from 16 • m in lead to 8 • m in silicon. With some assumptions on crater dimensions and shapes, these diameters convert to single-pulse mass removal values of 16 pg and 0.5 pg, respectively. These values correspond well to the assumptions we had made based on the previous experience of workers at Lincoln Laboratories, assumptions we used in estimating system performance in our Phase I proposal. It can be seen that they are in a good range for our proposed application of analyzing particles in the 1 to 10 • m diameter range. Interestingly, the single pulse mass removal with the microchip laser is similar to what is obtained with conventional LIBS systems using 1000X more pulse energy.

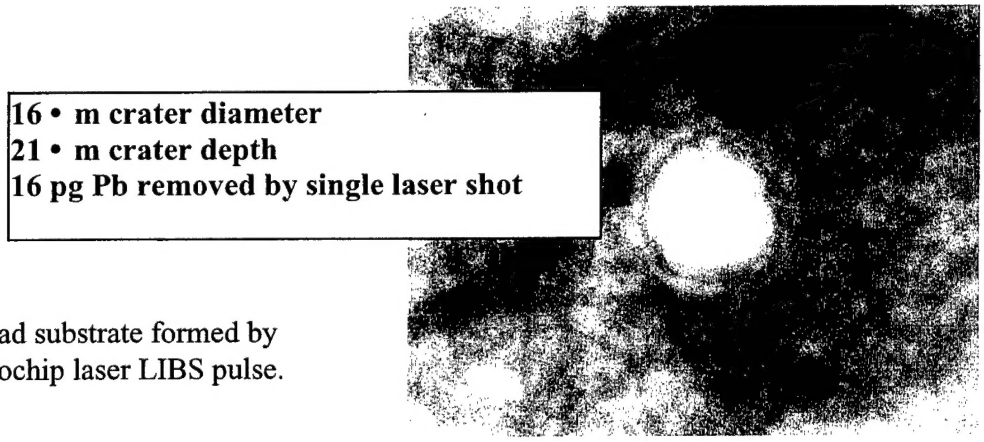

Figure 3. Crater in lead substrate formed by single microchip laser LIBS pulse.

Another characteristic of LIBS with microchip lasers, which we assume to be related to the small plasma dimensions and short lifetime discussed above, is the possibility that it is not necessary to time-gate the data acquisition system in order to discriminate against an initial emission dominated by continuum plasma emission. In the University of Florida laboratory setup, we could easily scan the field of view of the collecting optics and observe that the ratio of atomic line emission to this continuum emission could be varied substantially. This is an important observation for two reasons. First, of course, it is clearly advantageous to optimize the light collection into the spectrometer to maximize the ratio of atomic lines, carrying the information for analysis, to the background continuum. Second, the even more important optimization is one in which the fluctuations in background intensity are minimized. The short plasma lifetime combined with a relatively weak spectral contribution from the continuum background indicate that it is not necessary or even advisable to time-gate the detection. This is advantageous in terms of simplifying the detection approach and will make it easier to take advantage of the high repetition rate of these microchip lasers. Figure 4 shows spectra of a variety of materials obtained without time gating.

We have also made measurements of some fundamental plasma characteristics. The plasma temperature is difficult to characterize in a meaningful way without time resolution on the 0.1 ns scale. In spectra obtained without gating, strong atomic resonance lines are

heavily self-reversed and ionic lines are prominent indicating a temperature domain which is similar to what is observed in conventional LIBS, e.g., peaking around 10 – 30 kK. The critical difference is that the microchip laser plasma is of much smaller volume and, as indicated above, has a much shorter lifetime.

From the perspective of analytical spectrochemistry, the time-integrated emission spectra from the microchip LIB plasma exhibit very similar S/N to what is obtained with conventional LIBS. This is reasonable if one considers the complete vaporization of a small particle in either plasma; the larger volume of the conventional plasma actually serves to dilute the available atomic population while the microchip laser plasma is an exceptionally efficient point source emitter. The spectra in Figure 5 serve to emphasize this point, that microchip laser plasmas involve higher densities of analyte atoms, compressed into much smaller plasmas. Figure 5 shows the emission of the Zn

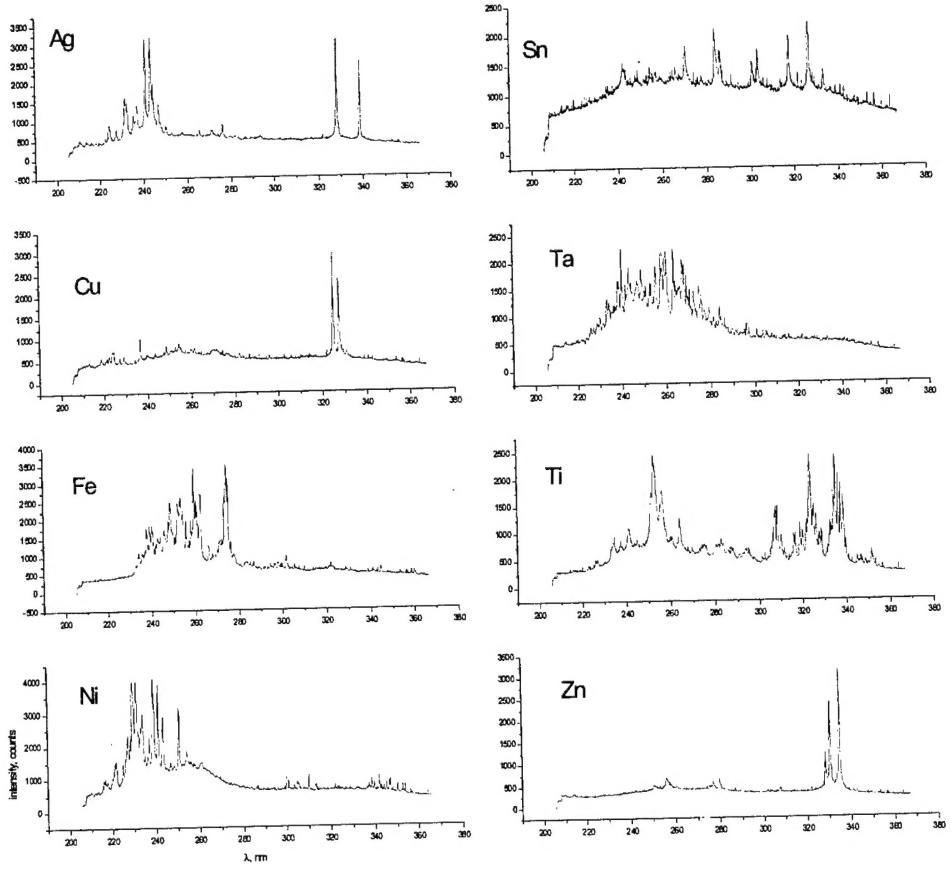

Figure 4. LIBS emission spectra of a variety of substrates, obtained at the University of Florida using the JDS Uniphase microchip laser and an Ocean Optics USB2000 miniature spectrometer.

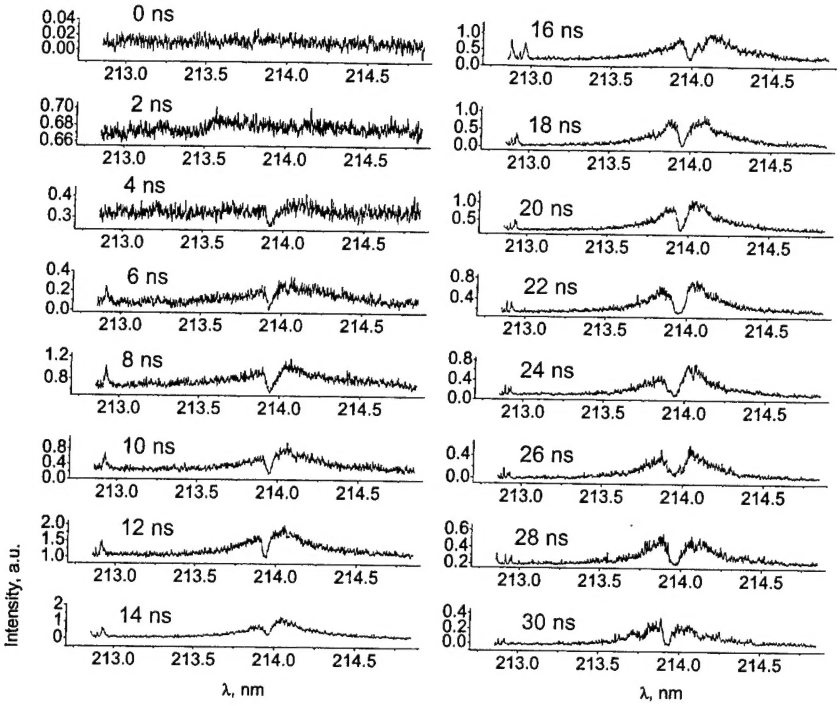

Figure 5. Spectra of microchip laser LIBS of the zinc neutral 213.9 nm line at different spectrometer gate delay times.

resonance line at 214 nm on a pure zinc sample as a function of delay in the spectrometer time gate. There is no time resolution since the gate was always longer than the less than 2 ns plasma lifetime, but as the delay increases one sees the line develop as the gate gradually encompasses the plasma emission. The interesting thing to note is that the Zn line is strongly broadened and self-reversed, just as one observes in conventional LIBS.

The results presented so far originated in the Winefordner group at the University of Florida. More recently, the Hahn group made measurements for aerosolized Bacillus licheniformis spores, using a conventional high power laser. These results are shown in Figure 6. The spores were suspended in purified water and then aerosolized using a pneumatic nebulizer into a stream of purified air. LIBS spectra were collected by creating a plasma directly in the aerosol stream and collecting light in a backscatter mode using a pierced mirror. Spectra were collected at a 5 Hz repetition rate using a 250 mJ/pulse 1064-nm Nd:YAG laser. Each individual spectrum was analyzed in real-time for the presence of calcium using the Ca II line at 393.366 nm, one of the more sensitive Ca lines. Based on the estimated solution concentration, nebulization rate, and co-flow air rate, the expected bioaerosol number density was several particles per cubic centimeter, which provides a single particle hit rate on the order of 10 particles per 1000 laser shots. Spectra were collected using a 0.275-m spectrometer and an intensified charge-coupled device (iCCD) array. The upper three spectra all correspond to identified individual spectra of single B. licheniformis spores.

The lower spectrum, not at the same scale as the single-shot spectra, is an ensemble-averaged calcium reference spectrum detailing the 393.366 and 396.847 nm emission lines.

The signal-to-noise ratio in the single-shot spectra, though not overly large, is adequate for detection and classification. In the light of the basic studies of relative mass ablation and LIBS signal intensities presented above, we can conclude that at least a high-power microchip laser has a good chance of exhibiting similar performance.

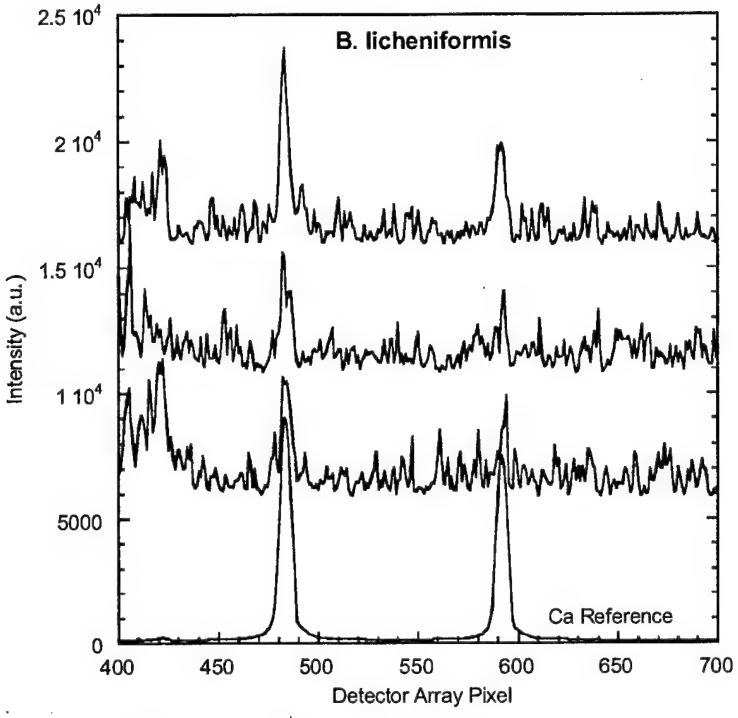

Figure 6. Conventional LIBS spectra of single bacteria spores,

Task 3. Assemble a particle beam LIBS test bed apparatus

The Aerodyne particle-beam test bed was originally assembled for the development and testing of instrument modules to be used with the Aerodyne aerosol mass spectrometer. It includes a vacuum system, a particle source, a LIBS detection system, LIBS excitation lasers, and a light scattering trigger laser system. The vacuum is supplied by two turbomolecular pumps backed by a diaphragm pump. The components of the particle source include a nebulizer for the formation of particles (initially, NaCl), a drying train, a differential mobility analyzer (DMA) to select a particular size range of particles, and an inlet orifice which determines the flow into the vacuum system. A small portion of the gas stream bypasses the instrument and is directed into a TSI model 3022A condensation particle counter, to measure the concentration of particles in the gas stream. The LIBS detection system is a miniature photomultiplier tube behind a sodium resonance line filter. The microchip laser used for the LIBS excitation tests was a Litton Poly-Scientific model with 11 microjoule pulse energy and an 8 kHz repetition rate. Preliminary tests were made using an

excimer laser with a much larger pulse energy and much slower repetition rate. The test bed has numerous ports to allow attachment of various instruments that sample, characterize or otherwise interact with beams of particles.

Task 4. Conduct experiments to support estimation of probability of single-particle detection

A key advantage of the device we are pursuing is that it analyzes particles one at a time, so that threat particles are not hidden in an average with a much larger number of benign, background particles. The number of particles per second we can analyze will be limited by the time for acquisition and analysis of LIBS spectra. As electronics and computers continue to advance, we can expect the number of particles analyzed per second to increase. We then must design the particle sampling apparatus so that it can deliver enough particles that the maximum analysis rate is reached. The number of particles giving LIBS signals per second can be increased in two ways: by increasing the flow through the preconcentrator, and thus the total number of particles being sent through the apparatus, or by increasing the probability that the LIBS laser hits an individual particle. There is no absolute requirement on either of these options, only the requirement that the result of both is the desired number of LIBS spectra per second.

Work under this task addressed the second issue, of increasing the probability that a given particle yields a LIBS spark, in two ways. One area of study was the variation of probability of LIBS sparks with the focusing parameters of the excitation laser. The second was that of triggering the microchip laser, so that eventually its pulses could be synchronized with the arrival of individual particles using laser light scattering.

Focal volume characterization experiments

Experiments in the first area were performed on the test bed apparatus described above, with a stream of NaCl particles produced from a test gas having a particle density of approximately $10^6/cm^3$. The exciting laser beam was directed across the particle beam, and focused to a point in the center of the beam. Emission at 590 nm from Na atoms was collected by an ellipsoidal reflector and focused through a narrow-band filter onto a miniature photomultiplier tube, the output signal from which was displayed on a digital storage oscilloscope. At the sampling location, 15 cm downstream from the outlet of the aerodynamic lens, the particle beam has a width of approximately 2 mm. (The width is somewhat variable, as beam divergence is dependent upon the shape of the particles -- non-spherical particles diverge more rapidly than do spherical particles. However, an upper limit of 3 mm is established by the size of the holes in the ellipsoidal reflector.)

Preliminary experiments were performed with a KrF excimer laser (MPB Technologies Inc. Model PSX-100, 248 nm, 2 millijoule/pulse) operating at 100 Hz. The laser beam was focused through a 38 mm fl lens to create LIBS sparks from an Al wire mounted at the position of the particle beam. Then the wire was removed, the system evacuated, and the particle beam turned on. These experiments produced definite, well-defined Na emission signals, at rates consistent with the expected size of the focal volume with power density high enough to give LIBS sparks. We also detected signals when the

particle beam was turned off, presumably from scattered 248 nm radiation that leaked through the 590 nm filter or from fluorescence within the filter caused by scattered UV laser light. However, the signals we attributed to Na emission from particles were four to ten times as intense as those "background" pulses.

The excimer laser was replaced by a microchip laser (Litton Polyscientific ML Series TO-3, 1064 nm, 11 microjoules/pulse) operating at 8 kHz, and the process was repeated. The laser beam was focused with a 10 mm fl lens to produce LIBS sparks on the alignment Al wire before the system was evacuated. This yields about as tight a focus as one can obtain with a simple lens, but subsequent optical analysis has shown that while the focal volume is much smaller than that of the lens used with the excimer laser, the peak power densities are still much smaller as well. When the particle beam was turned on, some weak and infrequent pulses were detected. However, they were weak enough that they were not easily distinguishable from the dark pulses from the photomultiplier. Our optical analysis leads us to the same conclusion, that although the rate of pulses due to Na LIBS emission from NaCl particles in the particle beam should be larger than that observed with the excimer laser, their intensity should be lower. Our analysis, in fact, is quite consistent with just the factor of somewhat less than 10 that would bring microchip laser LIBS pulse intensities down into the noise level. This strongly suggests that the advice we received before we started Phase I, that a high-power microchip laser would be needed, was indeed accurate.

Microchip laser triggering experiments

The second area of study was that of triggering the microchip laser, with the eventual goal of triggering on individual particles using laser light scattering. Such triggering is already a feature of the Aerodyne aerosol mass spectrometer, so much of the work involved in generating a scattering laser beam, detecting the scattered light, and translating that into a trigger pulse that can be used by another instrument has already been done. It is true, however, that our application would require significant adaptations of these technologies.

In our Phase I work, we wanted to concentrate on the issue of the time uncertainty, or jitter, between a trigger pulse input to a microchip laser and the resulting laser pulse. Microchip lasers are passively Q-switched, meaning that a layer of intracavity saturable absorber prevents lasing until a critical amount of energy has been deposited by the pump laser. This means that if the pump laser power is increased or decreased, the pulse energy remains the same, while the pulse repetition frequency increases or decreases. The pulse-to-pulse variation in intensity can be very small, a characteristic that can be very useful in applications such as LIBS. It might seem, however, that if our plan is to use the trigger signals from the light scattered from one or two laser diodes crossing the aerosol beam upstream of the LIBS excitation laser, a passively Q-switched microchip laser is not the right choice for that excitation laser. It turns out that generating a microchip laser pulse on demand is straightforward: one simply pulses the excitation laser. We had been led to expect by the manufacturers that for our off-the-shelf, low power Phase I microchip laser this could lead to jitter values as low as about 1 • s.

The system requirements and techniques for achieving short jitter times have been the subject of investigations by several research groups using Lincoln Laboratory microchip lasers. In our Phase I experiments, we were able to verify some of the keys to short jitter times learned by previous investigators. We used the Litton Poly-Scientific driver board adjusted to provide a pump diode current below its lasing threshold, and a pulse generator to supply a waveform that periodically brought it above threshold for the time needed to generate one pulse from the passively Q-switched microchip laser. We knew we wanted the DC level to be very close to the lasing threshold. We also found that raising the pump diode current well above its nominal DC level for the short time needed to pump the microchip laser yielded a substantial reduction in jitter time. Extrapolating to the rated maximum current suggested that an uncertainty of about 1 • s would indeed be the limit of the low power laser.

One way of looking at a pulse timing uncertainty of 1 • s is that it increases the odds of hitting an individual particle by more than two orders of magnitude over simply allowing the laser to free-run at, say 5 kHz. However, a 1 • s jitter also means that a 1um particle traveling at 2000 cm/s will have a position uncertainty of 20 • m, while the interaction region (focused laser beam waist) might be of order 10 • m wide. This means another increase of an order of magnitude in fraction of total particles detected should still be available, suggesting that reducing the trigger jitter to more like 0.5 • s should be our ultimate goal. We have learned that jitter times of less than 100 ns (0.1 • s) have been achieved repeatedly, but only with diode array pumping. Some commercial high-power devices do indeed use diode arrays, so this seems to fit well with our goal of transitioning to a high-power microchip laser.

In summary, triggering the laser pulse improves laser targeting along the axis of the particle beam. Improvements in all three dimensions can be achieved by optimizing the laser focusing and increasing laser power, while further improvements in the two transverse dimensions can come from better particle beam focusing. Our Phase I experiments suggest that the high-power microchip laser should meet our requirements both for accurate triggering and adequate pulse power, while we expect better particle beam focusing to come from the Phase II task which modifies the inlet and lens system to better match our application.

Task 5. Conceptual design of biological agent aerosol LIBS instrument

One important point to be made is that we expect that the parameters of size, weight, cost, power requirements, and robustness of a fully developed instrument to be better than those of Aerodyne's current commercial aerosol mass spectrometer. We should add that these aerosol mass spectrometers have been flown on aircraft, operated in mobile vans while carrying out real-time sampling while in motion, and used in remote locations including oceangoing ships. Therefore, we expect that there are no insurmountable hurdles, in either hardware and software, to a field device which works in an automated fashion and does not require an expert operator. Most of the hardware components, as well as the automated data analysis algorithms to process LIBS spectra and other measurements to identify target particles and discriminate against background signals, have been successfully used in other

applications. Therefore, most of the challenges in carrying this work forward are related to the particularly challenging application of biological agent detection.

A schematic of the proposed LIBS-based biothreat agent detection instrument is shown below in Figure 7. It includes a nozzle-inlet, aerodynamic lens collimator, laser scattering particle deteector and trigger, a microchip laser and a fiber-coupled silicon array-based spectrometer for the actual LIBS detection. The entire system will be pumped by a moderate sized turbomolecular pump – a choice made for convenience. Note also the proposed use of a virtual impactor-based pre-concentrator, a choice mandated by the detection requirements of 1 biothreat particle per liter of air. The proposed inlet system/pumping system is designed to work a gas flow of no more than 0.3 liters/min. A two stage preconcentrator will readily incorporate all the particles in a gas flow of 30 liters/min into an output flow of only 0.3 liters/min, ensuring that the detection system will sample ~30 particles/min at the required sensitivity levels. Suitable preconcentrators have been reported in the literature and will soon be commercially available.[17-19]

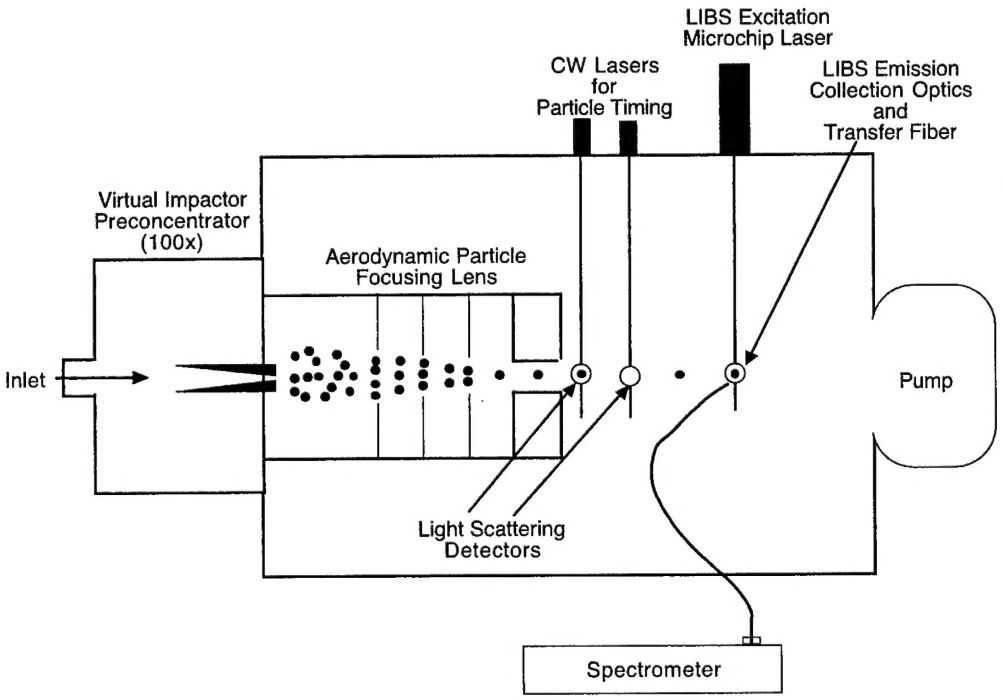

Figure 7. Conceptual design of particle beam microchip laser LIBS instrument.

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